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Technical Report No. 2

Pyrromethene–BF_2 Complexes as Laser Dyes: 2

by

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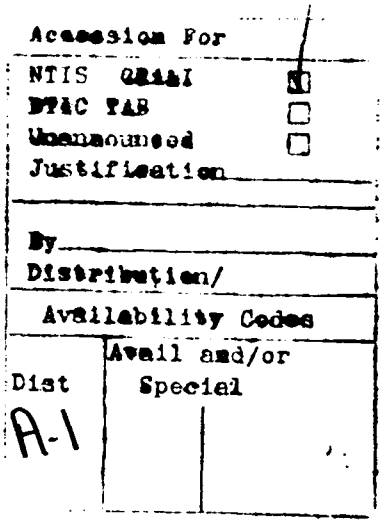


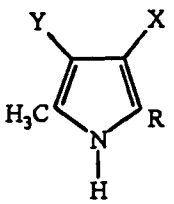
June 2, 1992

Pyrromethene–BF_2 Complexes as Laser Dyes: 2

Pyrromethene–BF_2 complexes (P–BF_2) **7** were obtained from α-unsubstituted pyrroles **5** by acylation and condensation to give intermediate pyrromethene hydrohalides **6** followed by treatment with boron trifluoride etherate. Conversion of ethyl α-pyrrolecarboxylates **4** to α-unsubstituted pyrroles **5** was brought about by thermolysis in phosphoric acid at 160 °C, or by saponification followed by decarboxylation in ethanolamine at 180 °C, or as unisolated intermediates in the conversion of esters **4** to pyrromethene hydrobromides **6** by heating in a mixture of formic and hydrobromic acids. Addition of hydrogen cyanide followed by dehydrogenation by treatment with bromine converted 3,5,3′,5′-tetramethyl-4,4′-diethylpyrromethene hydrobromide **9** to 3,5,3′,5′-tetramethyl-4,4′-diethyl-6-cyanopyrromethene hydrobromide **6bb**, confirmed by the further conversion to 1,3,5,7-tetramethyl-2,6-diethyl-8-cyanopyrromethene–BF_2 complex **7bb** on treatment with boron trifluoride etherate.

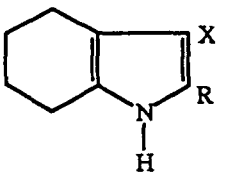
An alternation effect in the relative efficiency (RE) of laser activity in 1,3,5,7,8-pentamethyl-2,6-di-n-alkylpyrromethene–BF_2 dyes depended on the number of methylene units in the n-alkyl substituent, $-(CH_2)_nH$, to give RE ≥ 100 when n = 0, 2, 4 and RE 65, 85 when n = 1, 3. (RE 100 arbitrarily assigned to the dye rhodamine–6G). The absence of fluorescence and laser activity in 1,3,5,7-tetramethyl-2,6-diethyl-8-isopropylpyrromethene–BF_2 complex **7p** and a markedly diminished fluorescence quantum yield (Φ 0.23) and lack of laser activity in 1,3,5,7-tetramethyl-2,6-diethyl-8-cyclohexylpyrromethene–BF_2 complex **7q** were attributed to molecular nonplanarity brought about by the steric interference between each of the two bulky 8-substituents with the 1,7-dimethyl substituents. An atypically low RE 20 for a peralkylated dye without steric interference was observed for 1,2,6,7-bistrimethylene-3,5,8-trimethylpyrromethene–BF_2 complex **7j**. Comparisons with peralkylated dyes revealed a major reduction in RE for the six dyes **7u-z** lacking substitution at the 8-position.

Low laser activity RE was brought about by functional group (polar) substitution in the 2,6-diphenyl derivative **7l**, RE 20, and the 2,6-diacetamido derivative **7m**, RE 5, of 1,3,5,7,8-pentamethylpyrromethene–BF_2 complex (PMP–BF_2) **7a** and in 1,7-dimethoxy-2,3,5,6,8-pentamethylpyrromethene–BF_2 complex **7n**, RE 30. Diethyl 1,3,5,7-tetramethyl-8-cyanopyrromethene-2,6-dicarboxylate–BF_2 complex **7aa**, and 1,3,5,7-tetramethyl-2,6-diethyl-8-cyanopyrromethene–BF_2 complex **7bb**, offered examples of P–BF_2 dyes with electron withdrawing substituents at the 8-position. The dye **7aa**, λ_{las} 617 nm, showed nearly twice the power efficiency that was obtained from rhodamine B, λ_{las} 611 nm.



4 R = $CO_2CH_2CH_3$

5 R = H



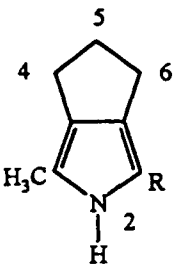
4l X = CH_3, R = $CO_2C_2H_5$

5h X = R = H

5l X = CH_3, R = H

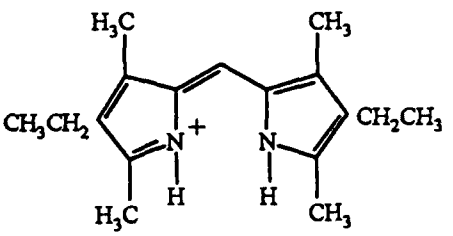
4,5	X	Y
a	CH_3	H
b	CH_3	CH_3
c	CH_3	CH_2CH_3
d	CH_3	$(CH_2)_2CH_3$
e	CH_3	$(CH_2)_3CH_3$
f	CH_3	$CH(CH_3)_2$
g	CH_3	$C(CH_3)_3$
k	CH_2CH_3	CH_2CH_3
o	C_6H5	CH_2CH_3
p	C_6H_5	C_6H_5
q	C_6H_5	$COCH_3$

5	X	Y
l	CH_3	C_6H_5
m	CH_3	$NHCOCH_3$
n	OCH_3	CH_3



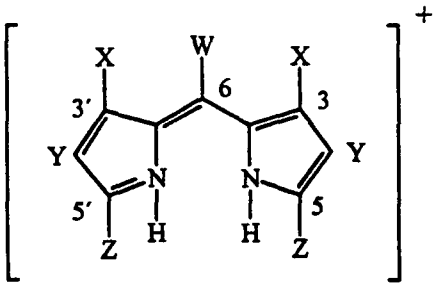
4j R = $CO_2C_2H_5$

5j R = H

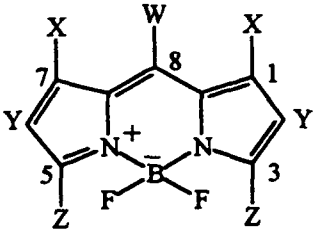


Br^-

9



6



7

6,7	W	X	Y	Z	A
a	CH_3	CH_3	H	CH_3	Cl
b	CH_3	CH_3	CH_3	CH_3	Cl
c	CH_3	CH_3	CH_2CH_3	CH_3	Cl
d	CH_3	CH_3	$(CH_2)_2CH_3$	CH_3	Cl
e	CH_3	CH_3	$(CH_2)_3CH_3$	CH_3	Cl
f	CH_3	CH_3	$CH(CH_3)_2$	CH_3	Cl
g	CH_3	CH_3	$C(CH_3)_3$	CH_3	Cl
h	CH_3	H	——$(CH_2)_4$——		Cl
i	CH_3	CH_3	——$(CH_2)_4$——		Cl
j	CH_3	——$(CH_2)_3$——		CH_3	Cl
k	CH_3	CH_2CH_3	CH_2CH_3	CH_3	Cl
l	CH_3	CH_3	C_6H_5	CH_3	Cl
m	CH_3	CH_3	$NHCOCH_3$	CH_3	Cl
n	CH_3	OCH_3	CH_3	CH_3	Cl
o	CH_2CH_3	CH_3	CH_2CH_3	CH_3	Cl
p	$CH(CH_3)_2$	CH_3	CH_2CH_3	CH_3	Cl
q	*c*-C_6H_{11}	CH_3	CH_2CH_3	CH_3	Cl
r	CH_2OCOCH_3	CH_3	CH_2CH_3	CH_3	Cl
s	*p*-$(CH_3)_2NC_6H_5$	CH_3	CH_2CH_3	CH_3	Cl
t	*p*-$CH_3OC_6H_5$	CH_3	H	CH_3	Cl
u	H	C_6H_5	CH_2CH_3	CH_3	Br
v	H	C_6H_5	C_6H_5	CH_3	Br
w	H	C_6H_5	H	CH_3	Br
x	H	CH_3	$C(CH_3)_3$	CH_3	Br
y	H	CH_2CH_3	CH_2CH_3	CH_3	Br
z	H	CH_3	CH_3	CH_3	Br
aa	CN	CH_3	$CO_2CH_2CH_3$	CH_3	Br
bb	CN	CH_3	CH_2CH_3	CH_3	Br